two classes of radicals would be expected to show opposite trends in their reactivities toward electron-rich and electron-poor alkenes. In this connection, Fischer et al.[20] have shown that the rate of addition of the nucleophilic *tert*-butyl radical (which has a high-lying SOMO, IP = 6.7 eV) tends to increase with an increase in electron affinity of the alkene, a result which indicates that the SOMO–LUMO interaction is important for these reactions. By way of contrast, it is the SOMO–HOMO interaction which should dominate the addition of the strongly electrophilic radical, n-$C_3F_7^{\bullet}$, to alkenes. This is demonstrated by the rough correlation ($\langle r \rangle$ = 0.94) between log k_{add} and IP for the seven terminal alkenes shown in Figure 1. This correlation is about as good as that of Fischer et al.[20] for log $k_{add}(Me_3C^{\bullet}$ + alkenes) vs electron affinity ($\langle r \rangle$ = 0.89) for a series of 21 alkenes. In both systems there are substantial deviations from the best straight line, which indicate that additional factors must control the reaction rates.[25] Experiments are underway to try to discover some of these "complicating" factors.

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Complete Sideband Suppression in Magic Angle Spinning Solid-State Nuclear Magnetic Resonance for Arbitrary Chemical Shift Anisotropies

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Magic angle spinning (MAS)[1,2] has become an indispensable method for obtaining high-resolution NMR spectra of dilute spins in solids. For spin-$^1/_2$ nuclei, the effect of MAS depends on the ratio $a = \omega_0\Delta\sigma/\omega_r$, where $\Delta\sigma = \sigma_{33} - \sigma_{iso}$ is the anisotropy of the chemical shift tensor, ω_0 the Larmor frequency, and ω_r the spinning frequency.[3,4] Fast MAS ($a \ll 1$) causes the static powder lineshape to collapse into a single resonance at the isotropic chemical shift $\omega_0\sigma_{iso}$. However, high spinning speeds present technical difficulties, may degrade cross polarization,[5,6] and also require small sample volumes. Slow MAS ($a > 1$) results in spinning sidebands at $\omega_0\sigma_{iso} \pm n\omega_r$ which often impair resolution. TOSS[7–10] (total sideband suppression) sequences have therefore been devised that achieve sideband cancellation for isotropic powder samples. However, TOSS also attenuates the centerband,[8,10,11] giving a residual centerband containing only 50% of the full intensity at $a \approx 2.5$ and zero intensity at $a \approx 4.5$, for $\eta = (\sigma_{22} - \sigma_{11})/\Delta\sigma = 1$. Here we present a new sideband suppression experiment which gives centerbands containing 100% of the full intensity *irrespective of the ratio a*.

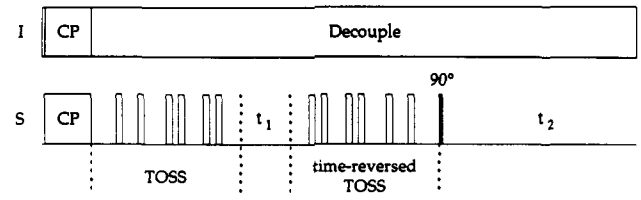

Figure 1. Pulse sequence for a MAS sideband suppression experiment for arbitrary ratios $a = \omega_0\Delta\sigma/\omega_r$. Cross polarization is followed by TOSS, an evolution period t_1, and then time-reversed TOSS. A 90° purging pulse selects one component of the magnetization for detection.

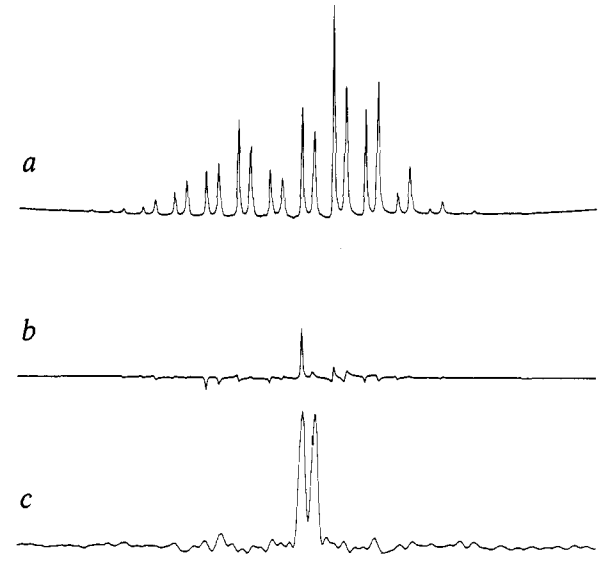

Figure 2. ^{31}P spectra of magnesium pyrophosphate, $Mg_2P_2O_7$, with a spectral width of 37.8 kHz at 121.5 MHz and $\omega_r/2\pi$ = 2 kHz. (a) Normal MAS spectrum. (b) TOSS spectrum obtained with the six-pulse sequence of Raleigh et al.[9] The centerbands are strongly attenuated since $a = \omega_0\Delta\sigma/\omega_r \gg 1$. (c) Spectrum recorded with the method of Figure 1. Here the isotropic peaks have equal areas since each contains the full MAS intensity of the corresponding sideband family.

The new method is shown in Figure 1, for dilute spins-$^1/_2$ S (such as ^{13}C or ^{31}P) coupled to abundant spins I (such as ^{1}H). We have demonstrated[12] that evolution under the [TOSS–t_1–reverse TOSS] sequence[13] is governed by the isotropic part of the chemical shift Hamiltonian alone and is thus independent of a. Therefore, the phase accumulated by the magnetization between the excitation sequence and the purging pulse of Figure 1 is $\varphi = \omega_0\sigma_{iso}t_1$, giving a signal immediately after the purging pulse proportional to cos φ, irrespective of the orientational distribution of crystallites. By stepping t_1 in the manner of a two-dimensional experiment, with increments Δt_1 small enough to sample the range of isotropic chemical shifts, and by using time-proportional phase increments (TPPI) to shift the origin of the frequency domain,[14,15] one can monitor the modulation indirectly through the amplitude of the first data point acquired. A real Fourier transformation

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with respect to t_1 gives a one-dimensional spectrum of full intensity centerband peaks, whatever the value of a.

In its simplest form, our method does not make full use of the available signal energy. Indeed, a spectrum $S(\omega_1,t_2=0)$ is identical to the *integral* over ω_2 of the two-dimensional spectrum $S(\omega_1,\omega_2)$. The integration adds up unwanted noise in addition to the signal energy which is concentrated in the sidebands at (known) equidistant frequencies in ω_2. More efficient use of the signal energy could in principle be made by sampling all rotary echoes in t_2 and co-adding the signals so obtained.

Experiments were performed on powdered magnesium pyrophosphate, $Mg_2P_2O_7$, which features two isotropic ^{31}P shifts separated by 750 Hz at 121.5 MHz on our Bruker MSL 300 spectrometer. Owing to the high values of the two different ratios a (for $\omega_r/2\pi$ = 2 kHz), a conventional TOSS spectrum (Figure 2b) shows severe intensity losses. In contrast, the spectrum acquired using the new method (but with a 90° excitation pulse instead of cross-polarization) has two equal intensity lines, as expected for a method which quantitatively reflects the stoichiometry of the sites (Figure 2c). A similar spectrum could be obtained by the PASS technique, albeit in a more cumbersome manner.[16]

Our new experiment is more powerful than TOSS since it not only suppresses the sidebands completely but also transfers the intensity of each sideband family into the corresponding centerband line. Moreover, in contrast to TOSS, this method is applicable to samples with an anisotropic distribution of crystallites, since the t_1 evolution does not depend on their orientation.[12] We use the acronym TIPSY (*t*otally *i*sotro*p*ic *s*pectroscop*y*) for experiments which incorporate this scheme for effecting evolution under the isotropic shifts alone.

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A One-Step Synthesis of the Ciclamycin Trisaccharide

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We have been investigating a glycosylation method that involves the use of anomeric phenyl sulfoxides activated with triflic anhydride[1] or catalytic triflic acid.[2,3] We now report that by using the sulfoxide method we are able to construct two glycosidic linkages sequentially in a single reaction. This has allowed us to synthesize the ciclamycin 0 trisaccharide stereoselectively from the component monosaccharides in one step.

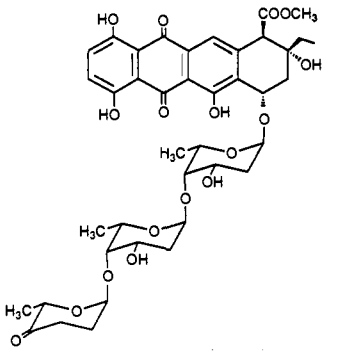
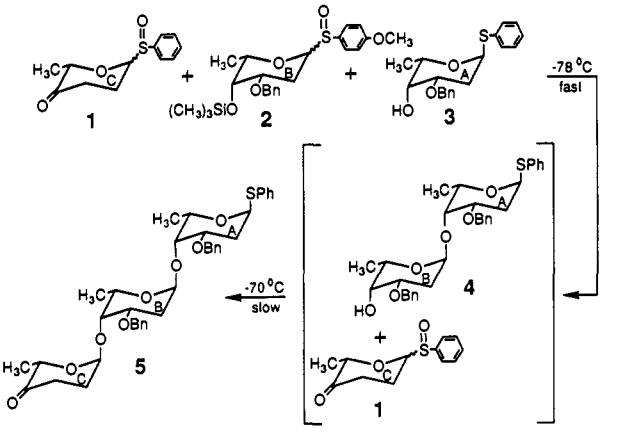


Figure 1. Ciclamycin 0.

Scheme I[a]



[a] Conditions: Premixed **1** (3.0 equiv), **2** (2.0 equiv), and **3** (1.0 equiv), Et_2O–CH_2Cl_2 (1:1), HC≡CCOOCH$_3$ (20.0 equiv), TfOH (0.05 equiv), −78 to −70 °C, 45 min, then quenched with saturated $NaHCO_3$ solution.

This synthetic approach grew out of mechanistic studies on the sulfoxide glycosylation reaction. We have found that the rate-limiting step in the reaction is triflation of the sulfoxide; therefore, the reactivity of the glycosyl donor can be influenced by manipulating the substituent in the para position of the phenyl ring (reactivity order: OMe > H > NO_2).[4,5] For perbenzylated glucose sulfoxides, the difference in reactivity is large enough that the *p*-methoxyphenyl sulfoxide can be selectively activated in the presence of an equimolar amount of the corresponding unsubstituted phenyl sulfoxide, *as long as only one-half of an equivalent of activating agent is present*. Both sulfoxides react, presumably,

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